FABRICATION AND PROPERTIES OF TRANSPARENT, CONDUCTIVE AND FLEXIBLE MULTI-WALLED CARBON NANOTUBES (MWCNTS)/EPOXY COMPOSITE FILM

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FABRICATION AND PROPERTIES OF TRANSPARENT, CONDUCTIVE AND FLEXIBLE MULTI-WALLED CARBON NANOTUBES (MWCNTS)/EPOXY COMPOSITE FILM

by

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LIST OF ABBREVIATIONS

Al	Aluminium
AFM	Atomic force microscopy
AHEW	Amine Hydrogen Equivalent Weight
Ca	Calcium
CNTs	Carbon nanotubes
DC	Direct Current
DGEBA	Diglycidyl Ether of Bisphenol A
DMA	Dynamic mechanical analysis
DNA	Deoxyribonucleic acid
DWCNTs	Double wall carbon nanotubes
EDS	Energy dispersive spectroscopy
EEW	Epoxide equivalent weight
EPD	Electrophoretic deposition
ESC	Electrostatic charge
FESEM	Field emission scanning electron microscope
FPD	Flat panel displays
FTIR	Fourier transform infrared spectroscopy
ITO	Indium tin oxide
IZO	Indium-doped zinc oxide
K	Potassium
L-MWCNTs	High aspect ratio MWCNTs
LB	Langmuir-Blodgett
LCD	Liquid crystal display

MAPLE	Matrix-assisted pulsed-laser evaporation
Mg	Magnesium
MMT	Montmorillonite
MWCNTs	Multi wall carbon nanotubes
Na	Sodium
NH_2	Amino group
N-H	Secondary amine unit
Ni	Nickel
O	Oxygen
OH	Hydroxyl unit
OLED	Organic light-emitting diodes
PC	Polycarbonate
PCBM	Phenyl-C61-butyric acid methyl ester
PE	Polyethylene
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PI	Polyimide
PLD	Pulsed-laser deposition
PMMA	Polymethyl methacrylate
PNCs	Polymer nanocomposites
PVA	Polyvinyl alcohol
RR-P3HT	Regioregular-poly-3-hexylthiophene
S	Sulphur
SSA	Specific surface area
SWCNTs	Single wall carbon nanotubes

S-MWCNTs	Low aspect ratio MWCNTs
T	Transmittance
TCFs	Transparent conductive thin films
TCO	Transparent conducting oxides
TEM	Transmission electron microscopy
TFPVs	Thin film photovoltaics cell
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
TV	Television
UV-vis	Ultraviolet–visible
XMS	X-ray Microanalysis System
TG/DTA	Thermo Gravimetry/Differential Thermal Analyzer
0-D	0-Dimensional
1-D	1-Dimensional
2-D	2-Dimensional
3-D	3-Dimensional
cPs	Centipoises
cm^{-1}	reciprocal centimeters
g/eq	gram per equivalent
g/ml	gram per millilitre
GPa	Giga Pascal
Hz	hertz
kHz	kilohertz
kN	Kilo Newton
kV	Kilovolt

meq/g	Milliequivalent per gram
m^2/g	square meters per gram
mPa.s	milli Pascal second
MPa	Mega Pascal
mm^2	square millimeter
mg	milligram
min	Minute
mm	Millimetre
nm	Nanometre
Pa.s	Pascal second
S/cm	Siemens per centimeter
t	Thickness
TPa	Tera Pascal
µm	Micrometre
^{o}	Degree
°C	Degree Celsius
Ω/sq	ohms per square
%wt	weight percent

LIST OF SYMBOLS

d	Thickness
D	Diameter
E	Young's modulus
E'	Storage modulus
F	Load
L	Length
δ	Loss factor
T_d	Onset Temperature of thermal decomposition
T_5	Temperature at 5 % weight loss
σ_{dc}	DC conductivity
Rs	Sheet resistance
σ_{op}	Optical conductivities
σ	Electrical conductivity
pv	Volume resistivity
Rv	Volume resistance
σ	Tensile strength
T_g	Glass transition temperature
ε	Strain at break
%	Percentage
C_{60}	Buckyball
λ	Lambda

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LIST OF SEMINAR AND EXHIBITION

Seminar

1. Mariatti, M., Saw, L.N. (2010). Tensile and Electrical Properties of Thin, Flexible and Transparent Multi-walled Carbon Nanotube/Epoxy Composites In: *Seminar Kebangsaan Aplikasi Sains & Matematik (SKASM) sempena Simposium Kebangsaan Sains Matematik ke-18 (SKSM 18)*, Johor Bahru, Malaysia, 8th -10th December 2010, pp.1-6.

Exhibition

1. Mariatti, M., Foo, Y. L. E., Saw, L.N., Voo, T.V., & Lim, C. S. (2011) A novel flexible epoxy thin film composites. In: *22nd International Invention, Innovation & Technology Exhibition (ITEX 2011*), Kuala Lumpur, Malaysia, 20th -22th May 2011.

FABRIKASI DAN SIFAT FILEM KOMPOSIT NANOTIUB KARBON DINDING BERBILANG/EPOKSI LUTSINAR, KONDUKTIF DAN MUDAH LENTUR

ABSTRAK

Dalam kajian ini filem nipis nanokomposit epoksi yang lutsinar optikal, konduktif dan mekanikal mudah lentur dihasilkan. Kajian ke atas sifat bagi perbezaan nisbah epoksi/agen pematangan, dua jenis nisbah aspek nanotiub karbon dinding berbilang (MWCNTs) dan pembebanan MWCNTs telah dijalankan. Keputusan ujian tegangan dan analisis dinamik mekanik (DMA) menunjukkan sifat sistem epoksi bergantung kepada nisbah epoksi-kepada-agen pematangan. Ianya menunjukkan spesimen dengan nisbah epoksi-kepada-agen pematangan 100: 45 (Sistem A) mempamerkan kekuatan tegangan, modulus Young dan modulus simpanan yang lebih tinggi berbanding dengan nisbah epoksi-kepada-agen pematangan 100: 60 (Sistem B). Dua jenis MWCNTs yang berlainan nisbah aspek dan pembebanan disebarkan dalam resin epoksi melalui proses ultrasonic dan diacuan mampat untuk menghasilkan filem nipis epoksi nanokomposit. Keputusan menunjukkan nanokomposit yang mengandungi MWCNTs dengan nisbah aspek yang rendah (S-MWCNTs) mempamerkan kekonduksian elektrik yang lebih bagus berbanding dengan nisbah aspek yang lebih besar (L-MWCNTs). Modulus Young, kekuatan tegangan dan kestabilan terma dalam filem nipis S-MWCNTs nanokomposit lebih tinggi jika dibandingkan dengan L-MWCNTs. Ini disebabkan penyebaran S-MWCNTs yang lebih bagus dalam resin epoksi. Rintangan helaian serendah 100 Ω/sq dengan lutsinar optikal lebih kurang 60 % pada 550 nm dicapai dengan penambahan MWCNTs ke dalam epoksi.

FABRICATION AND PROPERTIES OF TRANSPARENT, CONDUCTIVE AND FLEXIBLE MULTI-WALLED CARBON NANOTUBES (MWCNTS)/EPOXY COMPOSITE FILM

ABSTRACT

Optically transparent, conductive, and mechanically flexible epoxy thin films nanocomposite are produced in the present study. Investigations on the properties of different epoxy/hardener ratios, two different aspect ratios of multiwalled carbon nanotubes (MWCNTs) and MWCNTs loading in epoxy were carried out. The tensile test and dynamic mechanical analysis (DMA) results show that the properties of the epoxy system are governed by different resin/hardener ratios. It was shown that the specimens with an epoxy-to-hardener ratio of 100: 45 (Systems A) exhibit higher tensile strength, Young's modulus and storage modulus compared to an epoxy-to-hardener ratio of 100: 60 (System B). Two types of MWCNTs with different aspect ratios and loadings were dispersed in epoxy resin through an ultrasonication process and compression molded to form the epoxy thin films nanocomposite. Results showed that nanocomposites containing MWCNTs with a lower aspect ratio (S-MWCNTs) exhibit enhanced electrical conductivity compared to those with a higher aspect ratio (L-MWCNTs). Higher Young's modulus, tensile strength and thermal stability were observed in S-MWCNTs thin film nanocomposite if compared to those of L-MWCNTs. This behavior was associated with the better S-MWCNTs dispersion in the epoxy resin. A sheet resistance as low as 100 Ω/sq with nearly 60 % optical transparency in 550 nm is achieved with the addition of MWCNTs in epoxy.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The invention of the optically transparent, conductive and mechanically flexible electronic device could open a promising door for the next generation optoelectronic technology. Since the 1960s, the conducting indium tin oxide (ITO) has known as a key ingredient to offer electrical conductivity onto the optical transparent glass or polymeric thin film nanocomposites (Deshpande *et al*., 2008). However, the choice of this transparent conducting oxide is not promising. ITO thin film nanocomposites have shown several drawbacks, including high production costs and the scarcity of indium (Castro *et al*., 2009; Chan and Roussel, 2007). Furthermore, their rigidity made ITO coatings on flexible substrates performs reliability concern in certain applications (Chan and Roussel, 2007, Xu *et al*., 2009). As a consequence, new materials as replacements have been studied in the development of the flexible optical transparent conductive thin films (TCFs) nanocomposite. Carbon nanotubes (CNTs) are acknowledged as good replacements for ITO in TCFs nanocomposite fabrication (Chan and Roussel, 2007). The potential applications for TCFs nanocomposite range from transparent electrical shielding products to flexible video displays, including transparent monitors, touch screen panels, and laptop screens (Chan and Roussel, 2007).

CNTs/polymer thin film nanocomposites are commonly referred as potential materials to produce the TCFs nanocomposites. CNTs/polymer thin film nanocomposites combine the advantages of CNTs and polymeric materials, in which

CNTs exhibit higher strength (~100 times stronger than steel), modulus (about 1TPa) and thermal conductivity (about twice as high as diamond), excellent electrical capacity (1000 times higher than copper), thermal stability (2800°C in vacuum) and electrical properties (in the order of 10^3–10^4 S/cm) (Liao *et al*., 2004; Zhou *et al*., 2008). On the other hand, polymers present good flexibility, transparency, easy processing, and low cost (Peng, 2008). Besides that, CNTs have the superior combination of environmental stability, flexibility and high transparency at the visible wavelength characteristic compared to the conventional TCFs nanocomposite in the display industries (Gu and Swager, 2008; Saran *et al*., 2004). Furthermore, the CNTs were commonly deposited by spray coating and printing from suspension instead of the costly vacuum process (Gu and Swager, 2008). Thus, CNTs gives a great perspective for future flexible displays in the development of TCFs nanocomposite which more reliable in this application than the amorphous ITO. Compare to various types CNTs, multi wall carbon nanotubes (MWCNTs) has been widely used due to their lower price than single wall carbon nanotubes (SWCNTs) and double wall carbon nanotubes (DWCNTs). It is reported to show the highest potential of thermal and electrical conductivity enhancements in CNTs-based nanocomposites (Gojny *et al*., 2006).

1.2 Problem Statement

Fabrication of high quality, flexible, conductive, and transparent thin films remain challenging. Most of the previous efforts on these materials have focused on the properties of CNTs/thermoplastic thin film nanocomposites, such as polymethyl methacrylate (PMMA) and polyimide (PI) (Sellinger *et al*., 2006; Wu *et al*., 2010). The unique properties of thermoset polymers are excellent thermal stability and

optical properties, low viscosity and shrinkage, superiority in adhesion properties, good mechanical strength, erosion protection, and processing versatility. After realizing those unique properties, researchers have begun to carry out an increasing number of studies on thin films produced from epoxy systems (Shin *et al.*, 2009a). This rigid epoxy thin film provides good thermal properties and mechanical strength, but it can only be positioned in two dimensions (Li *et al.*, 2008a). Demand on flexible electronic technologies for a substrate which is able to fold and bent in three dimensions has increased. It is reported that this flexible substrate can decrease the failure under mechanical bending by absorbing internal stress, which is generated during processing (Li *et al.*, 2008a). This will increase the reliability of the thin film in roll-to-roll processing and reducing manufacturing costs.

1.3 Research Objectives

The objectives of this research work are:

1. To determine the effect of the different ratio of epoxy-to-hardener on the properties of transparent epoxy thin films.
2. To investigate the effect of different types of MWCNTs and contents on the transparency, electrical conductivity and tensile properties of the thin film nanocomposite materials.

1.4 Organization of Thesis

The thesis consists of five chapters. Chapter 1 contains an introduction of the TCFs nanocomposite, the project problem statements, research objectives and the arrangement of the thesis. Chapter 2 reports on a literature review that discusses on chemical structure and properties of CNTs, on thin film, TCFs nanocomposite and

CNTs in TCFs nanocomposite application. Chapter 3 describes the materials and experimental procedures details regarding the design, the optimization of the fabrication method and characterization techniques of epoxy thin film and MWCNTs/epoxy thin film nanocomposites. The results and discussion of the findings, including the surface morphology, mechanical electrical, thermal properties of the MWCNTs/epoxy thin film nanocomposites, are presented in Chapter 4. Chapter 5 is the final chapter that provides a foundation for the conclusions drawn out from the results. Moreover, the observations and suggestions for the future work to complement this research also presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the development of the optical flexible CNTs transparent conductive thin films (TCFs) nanocomposite is discussed. Various techniques fabrication, properties and application of optical flexible CNTs TCFs nanocomposite are also introduced. Finally, the development of the MWCNTs/epoxy thin film nanocomposites was explored as well.

2.2 Nanocomposites

Nanomaterials are typically categorized as 0-D (nanoparticles), 1-D (nanowires, nanotubes, and nanorods), 2-D (nanofilms and nanocoatings) or 3-D (bulk) (Ashby *et al*., 2009). Nanocomposites are nanomaterials that are created by introducing nanofillers into a macroscopic specimen material (Li *et al*., 2009). After adding nanofillers to the matrix material, the resulting nanocomposites may exhibit drastically enhanced properties (Li *et al*., 2009). Moreover, Michler, (2008) reported that the nanoscale reinforcement has an observable effect on the properties and the stability of polymers. For example, adding CNTs tends to improve the electrical and thermal conductivity. Other kinds of nanofillers may result in enhanced optical properties, dielectric properties, or mechanical properties such as stiffness and strength (Li *et al*., 2009). This has demonstrated a new class of composites, the polymer nanocomposites (PNCs) (Michler, 2008). PNCs are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small quantities (less than 5% by weight) of nano-sized fillers having high aspect ratios

with one dimension in the range of 0.1–100 nm. These PNCs are generally lightweight, require low filler content, and are often easy to process. They provide property enhancements extending orders of magnitude beyond those realized with traditional composites (Miller, 2008).

The development in PNCs technologies has been carried out as new classes of nanoscale fillers continue to emerge. By using nanofillers in a polymer matrix and achieving extraordinary properties is an area of active interest in nanocomposite technology (Kotsilkova & Pissis, 2007). Depending on the properties to be modified, the most suitable nanofiller have to be chosen to obtain the desired effect (Bellucci *et al*., 2010).

Nanofiller-filled polymers provide advantages over micron-filled polymers because they provide better resistance to degradation, and improvement in thermo-mechanical properties without causing a reduction in dielectric strength (Kozako *et al*., 2004; Ash *et al*., 2002). For example, Nelson and Fothergill, (2004) documented that an increase in dielectric strength and a reduction in space charge of nano-titanium dioxide (TiO_2) filled epoxy resin over micron size TiO_2 filled epoxy composites. These dielectric properties improvements could be due to several factors: (i) the large surface area of nanofillers altered the polymer behavior, (ii) polymer morphology changed due to the surfaces of particles, (iii) decrease in size of the particles causes the reduction of the internal field, (iv) change of the space charge distribution, and (v) a scattering mechanism (Ash *et al*., 2004; Ma *et al*., 2005; Nelson *et al*., 2002; Roy *et al*., 2005). According to Kotsilkova and Pissis, (2007) nanocomposites can exhibit novel and significantly improved properties not just

because of the small nanoscale size of the filler but also the chemical processes that occur at the nanofiller-matrix interface. Nanofillers in the polymer matrix showed two differences compared with conventional fillers (in the micron range) in polymer composites (Michler, 2008). These differences are due to the transition from micro-particles to nanofillers lead to a number of changes in physical properties. Firstly, the sizes of the nanofillers are comparable to the radius of gyration of the macromolecules in the polymer matrix, so that the morphological development of the polymer matrix can be substantially affected by the dispersed nanofillers (morphology under constraint condition). Secondly, the nanofillers have a high surface area-to-volume ratio, particularly when the size decreases below 100 nm and hence their properties are dominant by surfaces rather than bulk (Hosokawa *et al.*, 2007).

This high surface area to volume ratio means that for the same particle content, nanocomposites will have a much greater interfacial area than microcomposites. Since this interaction zone is much more extensive for nanocomposites than for microcomposites, it can have a significant impact on properties as shown in Figure 2.1 (Peukert *et al.*, 2003). As a consequence, the amount of modified polymer interfaces relative to the total volume will be significantly increased which corresponding to the transition from a polymer matrix material to a quasi-polymer interfacial material (Michler, 2008). For example, depending upon the strength of the interaction between polymer and particle, the interaction zone can have a higher or lower mobility than the bulk material and result in an increase or decrease in glass transition temperature (Ash *et al.*, 2002). Roy *et al.* (2005) stated that the dramatic improvement in electrical properties of the

nanocomposite was affected by the interactions between the nanoparticles surface and the matrix. They found that covalent bonding between the nanofillers and the matrix increases the temperature at which the breakdown strength decreases. The increase in the interfacial region in nanocomposites creates a zone of altered polymer properties, which reduces the dielectric permittivity of nanocomposites. The highest voltage endurance occurs for composites with strong covalent bonding between the matrix and the filler. Additionally, the nanofillers have dimensions below the critical wavelength of light makes them transparent, a property that makes them very attractive for applications in packaging, cosmetics, and coatings.

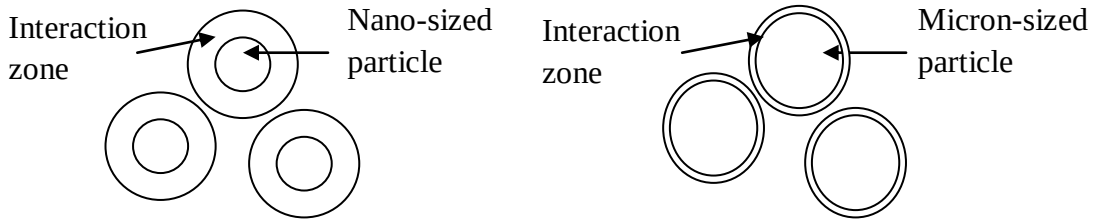

Figure 2.1: A comparison of particle and matrix interaction in nanocomposites and microcomposites (Li *et al*., 2009).

The commonly dispersed nanofillers in polymer matrices include: Silicon oxides (silica), Nanoclays (montmorillonite, hectorite, etc.), CNTs, etc. (Bellucci *et al*., 2010). Like most nanofiller, the nanoclay and silica were used to improve the barrier properties, modulus, mechanical properties of most composites, particularly stiffness and tensile strength. However, these types of nanofillers were unsuitable for the application that electrical conductivity was needed such as conductive plastics, nano-electronics. Thus, CNTs become the common nanofiller used to increase the conductive properties of the polymeric matrix.

2.2.1 Silicon Dioxide

Silicon dioxide is also known as silicon (IV). It is commonly called silica and become popular not just because of its hardness but also it can be easily found in nature as sand or quartz mineral (Whelan, 1994). The silica appears like a quasi-spherical shape with the diameter ranging from a few nanometers to 100 nm and thus the aspect ratio is close to 1. It can be used as filler in both thermoplastic and thermosetting polymer matrix with content in the range of 1–20 wt%. A compatible material is needed for better nanofillers dispersion. However, it depends on which type of polymer matrix (hydrophilic/hydrophobic) used in preparing the composite materials.

2.2.2 Clay

Clay is commonly called layered silicates which belong to the structure family known as phyllosilicates. This crystal structure consists with the prevailingly Si and O (base formula SiO_4) to form a tetrahedral structure (Rabová, 2009). Since each tetrahedral has an excess negative net electrical charge, the silicate must have that charge balanced by some metal cations to achieve an electrically neutral compound. The alkali or alkaline earth metals like magnesium (Mg), kalium (K), sodium (Na) and calcium (Ca) have purposed to bind together the different silicate tetrahedral structures. Montmorillonite (MMT), hectorite and saponite are the most common used of layered silicates in nanocomposites (Sinha Ray and Okamoto, 2003). These materials are widely used as electrical insulating materials due to their high aspect ratio (up to 1,000) and peculiar intercalation/exfoliation capability (Bellucci *et al.*, 2010).

2.2.3 Carbon Nanotubes

After the report on the discovery of " buckyball ", fullerence C_{60} molecule by Kroto *et al.* in 1985 there is huge increase in interest in their science. The C_{60} molecule exists in the discrete molecular form and consists of a hollow spherical cluster of sixty carbon atoms (Kakani & Kakani, 2006). Each molecule is composed of groups of carbon atoms that are bonded to one another to form both hexagon and pentagon geometrical configuration (Kakani & Kakani, 2006). In 1991, Sumio Iijima, a Japanese researcher working in NEC Laboratory explored a method to make fullerences using cathode arc discharge. He unexpectedly discovered a whole new class of fullerence called CNTs.

Since the discovery of CNTs, lots of researches have greatly stimulated this novel material in the field of physical, chemistry and material science. CNTs are cylindrical nanostructures with a diameter ranging from 1nm to several nanometers, and a length of tens of micrometers. They are made of graphene sheets wrapped into a hollow cylinder and capped by fullerence like structures (Ye and Sheu, 2007). CNTs are considered as a unique material with a lot of unusual properties such as hard and heat-conductive as diamonds, and many times stronger than steel at one sixth of the density. Unlike steel, nanotubes are flexible and elastic, bouncing back to their original shape after being bent or stretched. Besides that, it can be electrically conductors, insulator and semiconductor (Shim et *al*., 2008).

CNTs consisting of single and multiple concentric graphene cylinders such as single wall (SWCNTs), double-wall (DWCNTs), and multiwall (MWCNTs), depending on the shell number and how the graphene sheet rolled up itself

(Hernández-Pérez *et al*., 2008; Li *et al*., 2008b). SWCNTs possess a cylindrical nanostructure with a high aspect ratio, formed by rolling up a single graphite sheet into a tube. SWCNTs often capped at both ends, with outer diameters in the range from several nanometers up to 200 nm (O'Connell, 2006). The van der Waals forces keep the individual SWCNTs together, forming a triangular lattice with a lattice constant of 0.34 nm. DWCNTs are another new species in the family of carbon nanophase. They have the same small size as the SWCNTs but are stiffer and therefore, more appropriate as mechanical sensors (Kuzmany, 2006). Although DWCNTs are constructed from two SWCNTs with the same or different chiralities, the electronic properties of each nanotube within DWCNTs can be different from those of isolated SWCNTs (Banerjee *et al.,* 2009). MWCNTs are tiny electrodes made of carbon, metals or semiconducting materials having typical dimensions of 1-100 nm. The MWCNTs composed of individual SWCNTs concentrically with different diameters and separated by an interlayer distance of about 0.34 nm slightly larger than in graphite due to curvature (Maser, *et al.,* 2008). The length and diameter of the most inner tubes are similar to SWCNTs, the outer diameters, depending on the number of individual nanotubes, easily can reach values up to 20 or 30 nm (O'Connell, 2006; Maser *et al.*, 2009). These concentric nanotubes are held together by van der Waals bonding.

2.3 Thin Film Nanocomposites

Thin film technology is closely linked with nanotechnology, which is becoming one of the main areas in the new-generation manufacturing and precision engineering industries, especially in the manufacture of electronic, magnetic and optical devices (SreeHarsha, 2006). Thin film is considered as a layer of material

ranging from fractions of a nanometer (monolayer) to several micrometers in thickness (Tilman, 2010). Nowadays, there are strong requirements for the layer of materials to be transparent, conductive and flexible. It has also become an essential part of technologies to require both large area electrical contact and optical access in the visible portion of the light spectrum (Liu, 2007). For example, the resistivity of transparent conductive thin films must be made as low as possible in order to conserve energy, power and resources. For the past decades, transparent conducting oxides (TCO) become the only choice for the large flat screen high definition television, flat panel displays, hand-held smart displays, thin film solar cells, functional glass for window applications (SreeHarsha, 2006; Liu, 2007). One of the most widely used transparent conducting oxides is ITO.

ITO causes a great interest due to its transparency (higher than 80 % in the visible wavelength) and good electrical conductivity (Castro *et al*., 2009; Djaoued *et al*., 1997). Apart from that, ITO also has important properties such as high infrared reflectance, excellent substrate adherence and chemical inertness (Kim *et al*., 1999). Those properties have made ITO thin film nanocomposites adopted in many applications include plasma display panels, flat panel displays (FPD), liquid crystal display (LCD), organic light-emitting diodes (OLED) (Lee, *et al*., 2008). Nevertheless, ITO thin film nanocomposites can be prepared by many methods such as activated reactive evaporation, chemical vapor deposition, the sol-gel process (Ota *et al*., 2003; Biswas *et al*., 2003; Djaoued *et al*., 1997). However, those fabrication techniques involve vacuum and high temperature processes which are expensive and complicated (Chan and Roussel, 2007; Watcharotone *et al*., 2007). Furthermore, ITO coatings tend to undergo severe dimensional changes after mechanical bending or

hammering and thermal gradient (Chan and Roussel, 2007). All these drawbacks increase the interest for alternative material studied for ITO replacement, such as CNTs (Kaempgen *et al*., 2005).

2.4 CNTs/Thin Film Nanocomposites

CNTs are chosen to replace ITO in TCFs nanocomposite fabrication due to their ability to retain the same optical transparency and electrical conductivity properties, which are comparable with traditional ITO thin film nanocomposites (Pei *et al*., 2009). Furthermore, CNTs thin film nanocomposites exhibit comparable flexibility and environmentally resistant to ITO thin film nanocomposites. The carbon sources are cheaper and easy to obtain than indium; hence, CNTs become the only potential material in TCFs nanocomposite technology for replacement of ITO thin film nanocomposites in optoelectronic, durable transparent electrode application.

Dos Santos (2008) reported that there are two important factors that influence the load transfer in CNTs TCFs nanocomposite. The first factor is the strong interfacial bonding between a polymer matrix and CNTs and the second is a homogeneous dispersion of nanotubes throughout the polymer matrix. For examples, Ajayan *et al*., (2000) reported the weak interfacial bonding between the epoxy matrix and SWCNTs resulted in low performance nanocomposites. Agglomeration of nanotubes is reported to weaken the nanocomposite properties since agglomerated nanofillers often behave as micro or even macroscopic defects. Kim *et al*., (2007) reported that the higher surface energy of nanotubes leads to a heterogeneous dispersion in the polymer matrix and has negative effects on the properties of the resulting nanocomposites. Clearly, the state of dispersion of CNTs directly affects

the mechanical behavior of the materials (Song *et al*., 2005). To meet these challenges, a few successful approaches for the homogeneous dispersion have been explored by today researchers.

CNTs dispersion aids can be divided into five main types: (1) surfactant; (2) polymer wrapping; (3) direct dispersion of pristine or functionalized CNTs in organic solvent and water; (4) other dispersion aids such as DNA, protein and starch and (5) sonication (Hu *et al*., 2010; Suave *et al*., 2009). Using surfactant is the most widely used method for TCFs nanocomposite fabrication at high CNTs concentration. These are due to surfactant can be easily removed by subsequent washing of thin film after fabrication without affecting the thin film properties (Hu *et al.*, 2010). Polymer wrapping is another common method for CNTs dispersion, especially for CNT PNCs applications. Polymers are potentially assembled onto pristine CNTs through π-π stacking interactions, which preserve the CNTs intrinsic properties. For CNTs thin film nanocomposites applications, polymer-assisted dispersion is not preferred due to large size of polymers and the difficulty in removing the polymers after fabrication. Some methods have been proposed to remove polymers after CNTs thin film nanocomposites fabrication such as annealing or un-wrapping the polymers (Hu *et al*., 2010). Besides that, dispersed the functionalized CNTs in water is favorable due to the environmental friendly and biocompatible nature of water. Functionalization in acid condition can generate enough functional groups to facilitate the solubility of CNTs in water. However, dramatic amounts of defects are induced and cause matrix cracking, which leads to fiber debonding during mechanical testing (Hosur *et al.*, 2010). Other materials have been studied for dispersing CNTs such as DNA, protein and Nafion. DNA-assisted dispersion is of

particular significance due to its biological implications (Hu *et al*., 2010). According to Asada *et al*., (2010), the DNA wrapped CNTs are completely stable without unbound the DNA molecules. The DNA-CNTs are easily formed into uniform, desired-density and conductive networks of individual nanotubes (Asada *et al*., 2010). Centrifugation and sonication are the simple techniques that use high-intensity acoustic energy to create well dispersed CNTs solutions. During sonication, nanotubes entanglements are reduced. However, these techniques are reported to damage and degrade the structure of the CNTs which in turn could eventually shorten the length of the nanotubes (Hecht and Gruner, 2009). The sonication effect has been evaluated by Suave *et al*., (2009) that tensile strength of CNTs system increased after sonication at high amplitude for a short period of time.

2.4.1 Fabrication of Flexible CNTs TCFs Nanocomposite

Currently, several methods can be used in industrial and laboratory for TCFs nanocomposite fabrication. The solution-based deposition methods such as spin coating, dip-coating, slot coating, Langmuir-Blodgett (LB) and vacuum filtering are the most reliable and cost-effective methods to fabricate CNTs TCFs nanocomposite (Hu *et al*., 2010; Andrew Ng *et al*., 2008; Hecht and Gruner, 2009; Manivannan *et al*., 2010; Woo *et al*., 2007). Spin coating is preferred due to its simple processes, and it can be used directly on the substrate compared to vacuum filtration. The spin coating involved the high-speed spinning of the substrate (Hu *et al*., 2010). However, this simple solution deposition technique is hard to control the wetability on the substrate. As a consequence, the thin film that was fabricated is non uniform and become a problem for large production (Liu *et al*., 2010). This uneven thickness

would affect the TCFs nanocomposite electrical conductivity, transparency and mechanical properties.

Andrew Ng *et al*., (2008) reported on the use of dip coating in CNTs TCFs nanocomposite fabrication. They promoted that dip coating is scalable and become more promising for low cost and large-scale production of transparent and conductive coatings. The solution viscosity, concentration of the solution, the time of dip coating, the interaction between the substrate and the dispersion and the coating speed affect the thickness of the TCFs nanocomposite (Hu *et al*., 2010). However, both sides of the substrate are coated during the dip coating, become not practical for certain applications (Hu *et al*., 2010).

Slot coating is another process where a thin film (5–30 μm) of solution is applied evenly to the substrate surface through a slot die (Hecht and Gruner, 2009). This method yields thin films of high uniformity and high yield, and is a well known commercial process used in roll-to-roll manufacturing. However, the conductivity of thin films deposited by this method is limited by surfactant molecules remaining in the thin film structure after deposition. Therefore, all unwanted solubilization agents must be removed before processing (Hecht and Gruner, 2009).

LB is the method that needs the CNTs in hydrophobic behavior. This hydrophobic group enables a thin film to lay on a free surface of a subphase compound such as water (Armitage *et al*., 2004). This method is widely used by researchers to fabricate high quality CNTs TCFs nanocomposite because it is easier to control the thickness (Manivannan *et al*., 2010; Woo *et al*., 2007).

The vacuum filtration is also a widely used method to prepare CNTs TCFs nanocomposite specimen. However, this method shows few drawbacks where it is not suitable for large scale production in industrial due to the small and limited size of the membrane filtration (Manivannan *et al*., 2010). De *et al*., (2009) in their work develop the CNTs TCFs nanocomposite using vacuum filtration with transmittance and sheet resistance values of T=75 % and R_S= 80 Ω/sq.

Recently, an effective approach to produce flexible CNTs TCFs nanocomposite by a combination of electrophoretic deposition (EPD) and hot-pressing transfer was proposed by Pei *et al*., (2009). The CNTs TCFs nanocomposite obtained by this technique can achieve a sheet resistance of 220 Ω/sq and a transparency of 81 %, which satisfy the requirements set for touch screen application (Pei *et al*., 2009). It is reported that the pressing transfer lead to strong adhesion between the CNTs thin film and the polymer substrate. Since part of the CNTs thin film nanocomposites can be embedded into the polyethylene terephthalate (PET) substrate, the CNTs TCFs nanocomposite displays excellent flexibility. Besides, these EPD and hot-pressing techniques are simple, low cost, and have already been widely used in the industry. Therefore, this approach is reported well for the continuous production of homogeneous and large CNTs TCFs nanocomposite with desirable performance (Pei *et al*., 2009).

2.4.2 Properties of Flexible CNTs TCFs Nanocomposite

CNTs thin film nanocomposites are a novel 2D structure with a mixture of semiconducting and metallic tubes (Hu *et al*., 2010). CNTs thin film nanocomposites have the collective behavior of the individual tubes and the properties arising from

the tube-tube interactions (Hu *et al*., 2010). The properties of CNTs thin film nanocomposites, covering the electronic properties, optical transparency properties, chemical properties, and mechanical properties. According to Hu *et al*., (2010), the CNTs, doping level, tube length, thickness, and dispersion quality influenced the performance of transparent and conductive thin film nanocomposites. For example, Chien *et al.,* (2010) reported that the resistivity and transmittance are mainly affected by the thickness of the CNTs thin film nanocomposites. As the thickness of the CNTs is decreased, the thin film nanocomposite becomes less conductive and more transparent. Usually, the thin film nanocomposite DC conductivity can be calculated using equation (2.1) (Hu *et al*., 2010):

$$\sigma_{dc} = \frac{1}{\mathrm{Rs} \times d} \tag{2.1}$$

where σ_{dc} is the dc conductivity, Rs is the sheet resistance and d is the thickness of the thin films. The thickness of CNTs thin film nanocomposites is usually measured by an atomic force microscopy (AFM) image taken at the thin film edge. Equation (2.2) is used to measure the relationship between transmittance (T) and Rs of conductive and transparent CNTs thin film nanocomposites (Shin *et al.,* 2009b). This formula is suitable for thin film nanocomposites where the material must have absorption smaller than the reflectance, and has the thickness less than wavelengths.

$$T = \left(1 + \frac{1}{2\mathrm{Rs}} \sqrt{\frac{\mu_0 \sigma_{\mathrm{op}}}{\varepsilon_0 \sigma_{\mathrm{dc}}}}\right)^{-2} = \left(1 + \frac{188}{\mathrm{Rs}} \frac{\sigma_{\mathrm{op}}}{\sigma_{\mathrm{dc}}} (\lambda)\right)^{-2} \tag{2.2}$$

Here σ_{op} is the optical conductivities and λ is generally measured at 550 nm. The high value of the ratio $\sigma_{\mathrm{op}} / \sigma_{\mathrm{dc}}$ is needed for low Rs and high T properties (Nirmalraj *et al*., 2009). Lyons *et al*. (2008) in their work concluded that the dc conductivity depends on the nanotubes graphitization; however the conductivity decreases with

increasing thin film nanocomposite porosity and mean bundle diameter. Saran *et al*., (2004) reported that 1500 nm thick SWCNTs/PET thin film nanocomposites offer a sheet resistance of R_S~80 Ω/sq and T~80 %, which is comparable with commercial ITO/PET thin film properties (R_S~60-90 Ω/sq, T~80 %).

CNTs as one-dimensional crystalline carbon nanostructures have been used as extremely strong nano-reinforcements in TCFs nanocomposite fabrication due to its modulus on the order of 1 TPa, strength of 50-200 GPa, failure strains of up to 15 % CNTs (Coleman *et al*., 2006; Dumitrica *et al*., 2006; Treacy *et al*., 1996). With these unique properties make CNTs can easily be bended without breaking and will spring back to their original shape with no degradation in properties (Peltola *et al*., 2007). These become an essential property for CNTs TCFs nanocomposite fabrication, which required thin films to be mechanical flexibility, stretchability, and foldability. However, Buongiorno Nardelli *et al*., (2000) reported that under large geometrical deformations, a lot of defects formed and will significant affect the electrical response of CNTs. Thus, a lot of quantitative evaluations of the mechanical flexibility and sheet resistance of CNTs coating and ITO coating has been performed by cyclic and tensile strain test. For examples, Shin *et al*., (2009b) demonstrated that the SWCNTs/PET thin film shows more significant in sheet resistance than the commercial thin films of ITO/PET. The changes in sheet resistance were measured continuously to evaluate the specimen flexibility. They reported that the CNTs/coating showed only 20 % change in resistance after repeated bending and straightening and completely recovered after release, whereas ITO/PET thin films showed a > 48 fold increase in resistance after bending and become insulating after similar bending. Furthermore, the repeated bending cause cracks to occur and

degrades the ITO/PET thin films. Thus, the brittle ITO/PET thin films lead to catastrophic failures (Shin *et al*., 2009b). Weeks (2006) adopted the tensile strain test to evaluate the flexibility of CNTs/PET thin film and the resistance was measured in-situ with a digital multimeter. When the strain is above 5 %, the CNT/PET thin film change from elastic behavior to plastic deformation and the electrical resistance start to change. Only 14 % change in resistance was observed after 18 % change in the tensile strain which consider as smaller change than plastically deforming metal. Cairns *et al*., (2000) reported the onset of crack of ITO/PET thin film between 2 % and 2.5 % and the resistance was observed to increase sharply (>20000 %). The ITO failing catastrophically before 3 % tensile strain is reached.

2.4.3 Applications of Flexible CNTs TCFs Nanocomposite

CNTs thin film nanocomposites have found a large range of applications. The excellent mechanical, electrical conductivity and highly optical transparency properties of CNTs thin film nanocomposites have resulted in specific applications. There are many applications for CNTs thin film nanocomposites such as solar cell, OLEDs, electrostatic charge (ESC), touch screen, LCDs and EPD (Ulbricht *et al*., 2006; Koo *et al.*, 2007; Smith Jr. *et al*., 2008; Hecht *et al.,* 2009; Jang, 2006). A thin film solar cell is also called as thin film photovoltaics cell (TFPVs) (Adikaari *et al.*, 2010). CNTs have a superior electron transport, which makes the CNTs suitable to be used as filler in the organic photovoltaic device. It is able to increase carrier transport and as a transparent electrode to replace the ITO (Kymakis *et al.*, 2008). For example, Ulbricht *et al.*, (2006) reported that the use of strong transparent MWCNTs as the holes collecting electrode in polymer solar cells with regioregular-poly 3 hexylthiophene (RR-P3HT) as the donor material and phenyl-C61-butyric

acid methyl ester (PCBM) as the acceptor material. The material shows the efficiency of 1.32 % with sheet resistance of transparent CNT about 605 Ω/sq and it is reported to exhibit 30 times higher sheet resistance than that of ITO.

CNTs based OLEDs have rapidly reached large-scale commercialization due to its initial promise for low cost, large area, flexible displays and push by advances in efficiencies and operational lifetimes (Chien *et al.,* 2010). Usually, CNT transparent electrode is deposited on a transparent substrate to form the anode (Chien *et al.,* 2010). CNTs layer act as an electron injection enhancer at the cathodeorganic interface in OLED and were fabricated by using pulsed laser vaporization (Liu *et al*., 2009a). For example, Koo *et al.,* (2007) demonstrated that the luminance and current efficiency of polymer light-emitting diode improves with the increase in the doping amount of CNTs.

The ultralight weight, transparent, low colour, flexible, space-durable polymer thin films with inherent and robust electrical conductivity to dissipate ESC is needed for many applications such as advanced spacecrafts and roll-to-roll manufacturing facilities (Smith Jr. *et al*., 2008; Hu *et al*., 2010). The buildup of ESC without appropriate dissipation could cause catastrophic damage to the sensitive spacecraft electronic (Watson *et al.,* 2005). The surface resistivity (which relates to the surface conductivity) is required to dissipate ESC build-up on insulators (in the range from 10^6 to $10^{10}\,\Omega/\mathrm{sq}$) (Watson *et al*., 2005). It was found that surface conductivity of a CNTs coating is sufficient for ESC mitigation with negligible degradation in the optical properties. This thin film nanocomposites exhibit a high

degree of flexibility and mechanical robustness through harsh manipulation tests (Hu, *et al*., 2010).

Another application for transparent CNTs thin film nanocomposites is touch screens. Scientists predict that the first generation of transparent CNTs thin film nanocomposites was used as flexible electrodes in touch screens. Touch screens have rapidly expanded its market due to the popularity of the iPhone, amongst other devices (Hecht, 2009). There are various types of touch screens: four, five, or eight wires resistive touch screens, capacitive touch screens, acoustic touch screens, infrared touch screen, and others. Transparent and conductive electrodes are an essential component in most types of touch screen. The high-performance touch screens stringently require high T (>95 %) but tolerate of R_S of 400-600 Ω/sq (Hu *et al*., 2010). The mechanical robustness demonstrated by CNTs touch panels able to increase the lifetime and durability of current touch screens, while opening future applications in flexible and curved touch screens (Hu *et al*., 2010). The touch resistance of CNTs-CNTs versus CNTs-ITO could be better due to the absence of the possible heterojunction between CNTs and ITO (Hu *et al*., 2010). For examples, Hecht *et al., (*2009) demonstrated a prototype four-wire touch panels using a CNTs thin film as the top (touch) electrode. The CNTs refractive index of ~1.55 leads to CNTs touch panels with low reflection (<9 % over the visible range) and showed the total transmission of CNTs/PET thin film with 86 % over the visible and resistivity of 600 Ω/sq.

The application of transparent CNTs thin film nanocomposites on LCDs and EPD prototypes confirms the use of CNTs thin film nanocomposites for voltage-

driven displays (Hu *et al.,* 2010). Although the R_S (200 Ω/sq) with transmittance above 80 % for CNTs is much higher than for ITO (~20 Ω/sq), it has been demonstrated that high R_S does not prohibit the use of CNTs thin films in voltage driven devices. The response time in electrowetting displays, EPDs, and LCDs is not significantly larger than that for ITO or indium-doped zinc oxide (IZO)-based devices (Hu *et al.,* 2010). Because of their reflective mode, EPDs can only be used for e-paper or e-books and LCD for full colour video displays (Jang, 2006).

2.5 MWCNTs/Thin Film Nanocomposites

Today, most of the CNTs TCFs nanocomposites are made of SWCNTs. This is due to SWCNTs tend to be stronger than MWCNTs (Malik *et al*., 2008). On the other hand, the synthesis process of SWCNTs is expensive and cause the higher production cost (Resasco, *et al*., 2002). Furthermore, exfoliation of SWCNTs individually is difficult to be carried out during the purification process (Spitalsky *et al*., 2009). Thus, the use of MWCNTs is 500 times cheaper than SWCNTs at a similar purity (95 %) in the polymer matrix become more practically and rapidly growing (Postolek and Bogdal, 2010). MWCNTs present several complementary features with respect to SWCNTs, both for basic science and for applications. The MWCNTs can be produced in large quantities, which are an important aspect from the economic and scaling-up perspectives (Bautista-Quijanoa *et al*., 2010). The MWCNTs also can be grown without magnetic catalytic particles, which are certainly disturbing for magnetic, and probably for transport measurements, as well (Forro & Schonenberger, 2001). In addition, MWCNTs are considerably less agglomerated than SWCNTs and easier to form paper-like networks with homogeneous porosity (Spitalsky *et al*., 2009). The measurement of mechanical

properties of SWCNTs is generally more difficult than measuring those of MWCNTs, partly because the as-produced SWCNTs are held together in bundles by van der Waals forces and to separate them into individual SWCNTs is untrivial (Ma & Kim, 2011).

2.5.1 MWCNTs/Thermoplastic Thin Film Nanocomposites

Thermoplastic is also used with MWCNTs because it can be re-shaped, reheated into various forms without damaging the matrix properties. These behaviors allow the thermoplastic to be recyclable materials (Sheikh-Ahmad, 2009). Thermoplastic is the simplest molecular structure among the polymer matrix, consist of long molecular chains with no branches or cross-links as shown in Figure 2.2 (Buys and Oakley, 1994). Thermoplastic become softened or melted homogenized liquid when heated and become solidified hard when cooled.

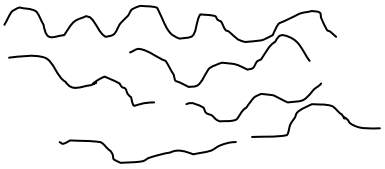

Figure 2.2: The polymer matrix molecular arrangement for thermoplastic.

Example of thermoplastic used in MWCNTs/polymer thin film nanocomposites fabrication is polyvinyl alcohol (PVA), polyethylene oxide (PEO) and PMMA. PVA is a water-soluble synthetic thermoplastic polymer. The hydrophilic property of PVA makes it permeable for water. It has an excellent thin film forming, emulsifying, adhesive properties and resistant to oil, grease and solvent. As for mechanical properties, it has high tensile strength and flexibility (Park, 2007). PEO is a synthetic thermoplastic polymer. It is soluble in water, methanol, benzene,